

## Unit-II Thermodynamics-II

**Syllabus:** Maxwell's Thermodynamic Relations: Thermodynamic variables, extensive and intensive variables. Derivation of Maxwell's thermodynamical relations (general relationship). Applications: specific heat equation for Van der Waals gas, Joule-Thomson-cooling and Joule-Thomson coefficient for perfect and Van der Waal gas. Clausius - Clapeyron's equation (first latent heat equation).

**Thermodynamic Potentials:** Internal energy, Enthalpy, Helmholtz free energy, Gibbs free energy. Significance of thermodynamic potentials. Relations of thermodynamical potentials with their variables. First and second order phase transitions.

### Thermodynamic variables:

The thermodynamic state of a substance is specified by some of its properties like pressure, volume, temperature, internal energy and entropy. These properties undergo a change when the system passes from one state to another. These variables are known as **thermodynamic variables** or co-ordinates. These are called **macroscopic co-ordinates**. They require the specification of few measurable properties of the system and do not require the knowledge of microscopic structure of matter composing the system.

### Extensive and Intensive Variables:

**An extensive variable** of a system is a macroscopic parameter which describes a system in equilibrium and which has a value equal to the sum of its values in each part of the system. The extensive variable depends upon the mass or the size of the substance present in the system.

Examples Mass, volume, internal energy, entropy, length, area, heat-capacity, electric charge, magnetization etc.

**An intensive variable** of a substance is a macroscopic parameter which describes the system in equilibrium and has the same value in any part of the system. It is independent of mass or size of the system. It is a characteristic of the substance present in the system.

Examples Pressure, temperature, viscosity, refractive index, density, specific volume, magnetic induction surface tension, electromotive force etc.

### Maxwell's thermodynamical relations:

From the two laws of thermodynamics, Maxwell was able to derive six fundamental thermodynamical relations. The state of a system can be specified by any pair of quantities viz pressure (P), volume (V), temperature (T) and entropy (S). In solving any thermodynamical problem, the most suitable pair is chosen and the quantities constituting pair are taken as independent variables.

From the first law of thermodynamics

$$dQ = dU + dW$$

$$dQ = dU + PdV \quad [ \because dW = F \cdot dx = P \cdot A \cdot dx = PdV ]$$

$$\therefore dU = dQ - PdV \text{-----(1)}$$

From the second law of thermodynamics

$$dS = \frac{dQ}{T} \Rightarrow dQ = T \cdot dS$$

Substituting the value of dQ in equation (1)

$$dU = TdS - PdV \text{-----(2)}$$

Considering S, U and V to be functions of two independent variables 'x' and 'y' [ here 'x' and 'y' can be any two variables out of P,V,T and S ]

$$dU = \left( \frac{\partial U}{\partial x} \right)_y dx + \left( \frac{\partial U}{\partial y} \right)_x dy$$

$$dS = \left( \frac{\partial S}{\partial x} \right)_y dx + \left( \frac{\partial S}{\partial y} \right)_x dy$$

$$dV = \left( \frac{\partial V}{\partial x} \right)_y dx + \left( \frac{\partial V}{\partial y} \right)_x dy$$

Substituting these values in equation (2)

$$\left( \frac{\partial U}{\partial x} \right)_y dx + \left( \frac{\partial U}{\partial y} \right)_x dy = T \left[ \left( \frac{\partial S}{\partial x} \right)_y dx + \left( \frac{\partial S}{\partial y} \right)_x dy \right] - P \left[ \left( \frac{\partial V}{\partial x} \right)_y dx + \left( \frac{\partial V}{\partial y} \right)_x dy \right]$$

$$\left( \frac{\partial U}{\partial x} \right)_y dx + \left( \frac{\partial U}{\partial y} \right)_x dy = \left[ T \left( \frac{\partial S}{\partial x} \right)_y - P \left( \frac{\partial V}{\partial x} \right)_y \right] dx + \left[ T \left( \frac{\partial S}{\partial y} \right)_x - P \left( \frac{\partial V}{\partial y} \right)_x \right] dy$$

Comparing the coefficients of dx and dy, we get

$$\left( \frac{\partial U}{\partial x} \right)_y = T \left( \frac{\partial S}{\partial x} \right)_y - P \left( \frac{\partial V}{\partial x} \right)_y \text{----- (3)}$$

$$\left( \frac{\partial U}{\partial y} \right)_x = T \left( \frac{\partial S}{\partial y} \right)_x - P \left( \frac{\partial V}{\partial y} \right)_x \text{----- (4)}$$

Differentiating equation (3) with respect to y and equation (4) with respect to x

$$\frac{\partial^2 U}{\partial y \partial x} = \left( \frac{\partial T}{\partial y} \right)_x \left( \frac{\partial S}{\partial x} \right)_y + T \frac{\partial^2 S}{\partial y \partial x} - \left( \frac{\partial P}{\partial y} \right)_x \left( \frac{\partial V}{\partial x} \right)_y - P \frac{\partial^2 V}{\partial y \partial x}$$

$$\frac{\partial^2 U}{\partial x \partial y} = \left( \frac{\partial T}{\partial x} \right)_y \left( \frac{\partial S}{\partial y} \right)_x + T \frac{\partial^2 S}{\partial x \partial y} - \left( \frac{\partial P}{\partial x} \right)_y \left( \frac{\partial V}{\partial y} \right)_x - P \frac{\partial^2 V}{\partial x \partial y}$$

The change in internal energy brought about by changing V and T whether V is changed by dV first and T by dT later or vice versa in the same. It means dU is a perfect differential.

$$\frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial y \partial x}$$

$$\begin{aligned} \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T \frac{\partial^2 S}{\partial y \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P \frac{\partial^2 V}{\partial y \partial x} \\ = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T \frac{\partial^2 S}{\partial x \partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P \frac{\partial^2 V}{\partial x \partial y} \end{aligned}$$

Simplifying

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x \dots\dots\dots(5)$$

Here x and y can be any two variables out of P, V, T and S. It is the general Maxwell's thermodynamic equation.

**Applications: specific heat equation for Van der Waals gas**

**Prove that**  $C_P - C_V = R \left(1 + \frac{2a}{VRT}\right)$

The specific heat of gas at constant pressure is given by

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P \quad \text{since } \partial Q = T \partial S$$

And specific heat at constant volume is

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V \quad \text{since } \partial Q = T \partial S$$

Now, if the entropy S is regarded as a function of T and V and dS is a perfect differential

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\ \therefore \left(\frac{\partial S}{\partial T}\right)_P &= \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_P + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad \text{Or} \\ T \left(\frac{\partial S}{\partial T}\right)_P &= T \left(\frac{\partial S}{\partial T}\right)_V + T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad \text{but} \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V \quad \text{from Maxwell's 2nd equation} \\ \therefore T \left(\frac{\partial S}{\partial T}\right)_P - T \left(\frac{\partial S}{\partial T}\right)_V &= T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \\ C_P - C_V &= T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \dots\dots\dots(1) \end{aligned}$$

For a gas obeying Vander Waal's equation, we have

$$\left(P + \frac{a}{V^2}\right) (V - b) = RT \dots\dots\dots(1)$$

Where a and b are constants and the other quantities have their usual meaning. Equation (2) can be written as

$$\left(P + \frac{a}{V^2}\right) = \frac{RT}{(V - b)} \dots\dots\dots(3)$$

Differentiating equation (3) w.r.t T, Keeping the volume constant

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{(V-b)}$$

Differentiating equation (3) w.r.t T, Keeping the pressure constant

$$\left(0 - \frac{2a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P = \frac{RT}{(V-b)^2}\left(\frac{\partial V}{\partial T}\right)_P + \frac{R}{(V-b)} \quad \text{Or}$$

$$\left(\frac{\partial V}{\partial T}\right) \left[\frac{RT}{(V-b)^2} - \frac{2a}{V^2}\right] = \frac{R}{(V-b)} \quad \text{Or}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\frac{R}{(V-b)}}{\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^2}\right]}$$

Substituting these values of  $\left(\frac{\partial P}{\partial T}\right)_V$  and  $\left(\frac{\partial V}{\partial T}\right)_P$  in equation (1) we get,

$$\begin{aligned} C_P - C_V &= \frac{T \left(\frac{R}{(V-b)}\right) \frac{R}{(V-b)}}{\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^2}\right]} = \frac{R \frac{RT}{(V-b)^2}}{\left[\frac{RT}{(V-b)^2}\right] \left[1 - \left(\frac{2a}{V^2}\right) \frac{(V-b)^2}{RT}\right]} \\ &= \frac{R}{\left[1 - \left(\frac{2a}{V^2}\right) \frac{(V-b)^2}{RT}\right]} \end{aligned}$$

Compared to V, b is too small and may be neglected.

$$\therefore C_P - C_V = \frac{R}{\left[1 - \left(\frac{2a}{V^3}\right) \frac{V^2}{RT}\right]} = \frac{R}{\left[1 - \left(\frac{2a}{RTV}\right)\right]} = R\left(1 - \frac{2a}{VRT}\right)^{-1}$$

Expanding binomially and neglecting a in higher powers, as a is very small as compared to V, we get

$$C_P - C_V = R\left(1 + \frac{2a}{VRT}\right)$$

### Joule-Thomson-cooling:

As we know, in Joule-Thomson porous plug experiment, if a gas at constant high pressure is forced through a porous plug to a region of constant low pressure, the temperature of escaping gas changes. This is called **Joule-Thomson effect**.

Due to throttling, the gas suffers expansion. Although there is a pressure difference on two sides of the porous plug, the enthalpy H of the gas remains constant. This is the necessary condition i.e.

$$H = U + PV = \text{a constant}$$

$$dH = dU + PdV + VdP = 0$$

$$\text{But } dQ = dU + PdV \quad (\text{I law of Thermodynamics})$$

$$\text{also } dQ = T.dS \quad (\text{II law of thermodynamics})$$

$$\therefore dQ = T.dS + VdP = 0 \dots \dots \dots (1)$$

Now dS being a perfect differential and S is a function of P and T i.e. S=f(P, T), we have

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad \text{substituting this in equation (1)}$$

$$T \left(\frac{\partial S}{\partial T}\right)_P dT + \left[ T \left(\frac{\partial S}{\partial P}\right)_T + V \right] dP = 0$$

$$\text{Now, } C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P \quad \text{since } \partial Q = T \partial S$$

where  $C_p$  is specific heat at constant pressure.

$$\therefore C_P dT = - \left[ T \left(\frac{\partial S}{\partial P}\right)_T + V \right] dP \quad \text{----- (2)}$$

According to Maxwell's fourth thermodynamical relation

$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore C_P dT = \left[ T \left(\frac{\partial V}{\partial T}\right)_P - V \right] dP \quad \text{OR}$$

$$dT = \frac{1}{C_P} \left[ T \left(\frac{\partial V}{\partial T}\right)_P - V \right] dP \quad \text{----- (3)}$$

### Joule-Thomson coefficient ( $\mu$ ) for perfect and Vander Waals gas:.

The Joule-Thomson coefficient ( $\mu$ ) is given by

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P} \left[ T \left(\frac{\partial V}{\partial T}\right)_P - V \right]$$

Now,  $\left(\frac{\partial V}{\partial T}\right)_P = \alpha V$  where  $\alpha$  is the coefficient of increase of volume at constant pressure,

because  $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$

$$\therefore \text{equation (3) becomes } dT = \frac{V}{C_P} [\alpha T - 1] dP \quad \text{----- (4)}$$

Equation (4) gives the change in temperature due to Joule-Thomson effect.

Here  $dP$  represents a fall in pressure in porous plug experiment and it is always a negative quantity All other quantities in equation (4) are positive. Hence

- There is cooling effect i.e.  $dT$  is negative if  $(\alpha T - 1)$  is + ve or  $T > 1$ .
- There is neither a cooling nor a heating effect i.e.  $dT = 0$  when  $(\alpha T - 1) = 0$  or  $\alpha T = 1$
- There is a heating effect i.e.  $dT$  is positive if  $(\alpha T - 1)$  is - ve or  $T < 1$

Let us apply the thermo dynamical treatment of heating and cooling effect to a perfect gas and Vander Walls gas.

**For a perfect gas:** According to perfect gas equation  $PV = RT$

At constant pressure  $P \partial V = R \partial T$

$$\therefore \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \quad \text{Or } T \left(\frac{\partial V}{\partial T}\right)_P = \frac{RT}{P} = V$$

$$\text{Hence } T \left[ \left( \frac{\partial V}{\partial T} \right)_P - V \right] = 0$$

using equation (3) we have for a perfect gas,  $dT = 0$

In other words, there is no Joule-Thomson effect for a perfect gas. Hence, the porous plug experiment provides us a method to decide whether the given gas is perfect or not. For a perfect gas, the Joule-Thomson coefficient ( $\mu$ ) is zero.

$$\therefore \mu = \left( \frac{\partial T}{\partial P} \right)_H = \frac{1}{C_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right] = 0$$

**For Vander Walls gas:** Van der Waals equation for one mole of a real gas is given by

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT \dots \dots \dots (1) \quad \text{Or}$$

$$PV = -Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

Since both the Van der Waals' constants  $a$  and  $b$  are very small quantities, their product  $ab$  is very small as compared to  $V^2$  and hence  $\frac{ab}{V^2}$  can be neglected.

$$\therefore PV = -Pb + \frac{a}{V} = RT$$

Differentiating both sides with respect to  $T$ , keeping  $p$  constant, we get.

$$P \left( \frac{\partial V}{\partial T} \right)_P - \frac{a}{V^2} \left( \frac{\partial V}{\partial T} \right)_P = R \quad \text{Or}$$

$$\left( \frac{\partial V}{\partial T} \right)_P \left\langle P - \frac{a}{V^2} \right\rangle = R \quad \text{Or}$$

$$\left( \frac{\partial V}{\partial T} \right)_P = \frac{R}{\left\langle P - \frac{a}{V^2} \right\rangle} \dots \dots \dots (2)$$

From equation (1)

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \text{Substitute the value of } P \text{ in equation (2)}$$

$$\begin{aligned} \left( \frac{\partial V}{\partial T} \right)_P &= \frac{R}{\left\langle \frac{RT}{V-b} - \frac{a}{V^2} - \frac{a}{V^2} \right\rangle} = \frac{R}{\left\langle \frac{RT}{V-b} - \frac{2a}{V^2} \right\rangle} = \frac{R(V-b)}{\left\langle RT - \frac{2a(V-b)}{V^2} \right\rangle} \\ &= \frac{R(V-b)}{\left\langle RT - \frac{2a}{V} \right\rangle} \quad \text{since } b \text{ is very small, } V-b = V \end{aligned}$$

$$\begin{aligned} \therefore T \left( \frac{\partial V}{\partial T} \right)_P &= \frac{RT(V-b)}{\left\langle RT - \frac{2a}{V} \right\rangle} = \frac{V-b}{\left\langle 1 - \frac{2a}{VRT} \right\rangle} \\ &= (V-b) \left( 1 - \frac{2a}{VRT} \right)^{-1} \\ &= (V-b) \left( 1 + \frac{2a}{VRT} \right) \end{aligned}$$

Neglecting squares and higher powers of  $\frac{2a}{VRT}$  as  $\frac{2a}{VRT} \ll 1$

$$\begin{aligned} \therefore T \left( \frac{\partial V}{\partial T} \right)_P &= (V - b) \left( 1 + \frac{2a}{VRT} \right) \\ &= V - b - \frac{2a(V - b)}{VRT} \end{aligned}$$

$$= V - b + \frac{2a}{RT} \quad [ \text{as } b \text{ is very small } V-b=V ]$$

$$\therefore T \left( \frac{\partial V}{\partial T} \right)_P - V = \frac{2a}{RT} - b \quad \dots \dots \dots (3)$$

According to Joule-Thomson effect, the change in temperature

$$dT = \frac{1}{C_P} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right] dP$$

Where  $C_P$  is molar specific heat at constant pressure

Substitute the value of  $\left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right]$  from equation (3), we get

$$\begin{aligned} dT &= \frac{1}{C_P} \left[ \frac{2a}{RT} - b \right] dP \\ dT &= \frac{dP}{C_P} \left[ \frac{2a}{RT} - b \right] \quad \dots \dots \dots (4) \end{aligned}$$

Equation (4) gives the change in temperature for Van der Waals gas. i.e. real gas due to Joule Thomson effect. Thus, we conclude that,

(i) if  $\frac{2a}{RT} >$

$b$  i.e.  $T$  is less than  $\frac{2a}{RT}$ , then  $\partial T$  is positive. Since  $\partial P$  is negative. Hence there will be a cooling effect.

(ii)

if  $\frac{2a}{RT} <$

$b$  i.e.  $T$  is greater than  $\frac{2a}{RT}$ , then  $\partial T$  is negative. Since  $\partial P$  is positive. Hence there will be a heating effect.

(iii) if  $\frac{2a}{RT} = b$  or  $T = \frac{2a}{RT}$ , then  $\partial T = 0$ , there will be no change in temperature.

### Thermodynamic Potentials:

The state of a system can be completely described by any two of the five state variables P,V,T,S and U. Out of these, U the internal energy state variable is determined by using the remaining four as proved below:

According to first law of thermodynamics,  $dQ = dU + PdV$  and from the second law of thermodynamics,  $dQ = TdS$

$$dU + PdV = TdS \quad \text{or} \quad dU = TdS - PdV$$

Thus, U can be eliminated and we are left with four state variables P, V, T and S only. This is the reason, why only four state variables are defined. Taking two of the four state variables P,V,T and S at a time, there are six possible pairs, i.e. (P, V), (P, T), (P, S), (V, T), (V, S) and (T, S). The pair (P, V) is

connected with composite and in exact differential quantity  $dW$  as  $dW = PdV$  and pair  $(T, S)$  with  $dQ$  as  $dQ = Tds$ . Hence these two pairs can be eliminated. Thus, we are left with four pairs of thermodynamical variables  $(P, T)$ ,  $(P, S)$ ,  $(V, T)$  and  $(V, S)$ . Corresponding to each pair, we can write a thermodynamical relation. These four thermodynamical relations are known as **Maxwell's thermodynamic potentials**. There are four thermodynamic potentials

(i) Internal energy,  $U$  (ii) Enthalpy  $H = U + PV$

(iii) Helmholtz free energy,  $F = U - TS$  and (iv) Gibbs function  $G = U + PV - TS$

Each of Maxwell's four thermodynamical relations can be derived from one of these thermodynamic potentials  $U$ ,  $H$  and  $G$ . Hence, only four thermodynamic potentials are defined.

**1, Internal Energy  $U$ :** The internal energy or the intrinsic energy is the total energy of a system. According to the first law of thermodynamics,

$$dQ = dU + dW = dU + PdV$$

$$\therefore dU = dQ - PdV \dots \dots \dots (1)$$

From second law of thermodynamics,

$dQ = TdS$  substituting for  $dQ$  in eqn. (1)

$$dU = TdS - PdV \dots \dots \dots (2)$$

This equation gives the change in internal energy of the system in terms of four thermodynamical variables  $P$ ,  $V$ ,  $T$  and  $S$ . Internal energy ( $U$ ) is called first thermodynamical potential.

(a) For an adiabatic process:  $dQ = 0 \therefore dU = -PdV$

i.e. the work done by the system in an adiabatic process is at the expense of its internal energy.

(b) For an isochoric adiabatic process:  $dV = 0$  and  $dQ = 0 \therefore dU = 0$  or  $U = a \text{ constant}$ .

i.e. the internal energy of system remains constant in an isochoric adiabatic process.

**2. Enthalpy  $H$ :** This is known as the total heat and is given by  $H = U + PV$

As  $U$ ,  $P$  and  $V$  are state variables,  $H$  is also a state variable.  $H$  has dimensions of energy. If the system undergoes an infinitesimal reversible process,

Then change in enthalpy  $dH = dU + PdV + VdP$

$$\text{But } dU = TdS - PdV$$

$$\therefore dH = TdS + VdP \dots \dots \dots (3)$$

(a) For reversible isobaric process :  $dP = 0$ ,  $dH = Tds = dQ$

i.e. for an isobaric process, the change in enthalpy is equal to the heat absorbed.

(b) For an isobaric adiabatic process  $dP = 0$ ;  $dQ = 0 \therefore dH = 0$  or  $H = a \text{ constant}$

i.e. enthalpy remains constant in a reversible isobaric adiabatic process.

**3. Helmholtz Free Energy  $F$ :** Helmholtz free energy is defined as  $F = U - TS$



As U, T and S are state variables, F is also a state variable. F has dimensions of energy. According to first and second law of thermodynamics,

$$dU = TdS - dW$$

If the system is maintained at a constant temperature by exchanging heat continuously with the surrounding, then,  $TdS = d(TS) \therefore dU = d(TS) - dW$  or

$$d(U - TS) = -dW \quad \text{or} \quad dF = -dW \dots \dots \dots (4)$$

where  $F = (U - TS)$  is known as **Helmholtz free energy or Helmholtz work function**.

$$\text{Now } dF = d(U - TS) = dU - TdS - SdT$$

$$\text{But } dU = TdS - PdV$$

$$\therefore dF = -PdV - SdT \dots \dots \dots (5)$$

This equation gives the change in Helmholtz free energy during an infinitesimal reversible process.

**(a) For reversible isothermal process:**  $dT = 0 \therefore dF = -PdV$  or  $PdV = -dF$

Thus, the work done in a reversible isothermal process is equal to the decrease in Helmholtz free energy.

**(b) For isothermal isochoric process:**  $dT = 0$  and  $dV = 0 \therefore dF = 0$  or  $F = a \text{ constant}$

i.e. the Helmholtz free energy remains constant during isothermal isochoric process..

**4. Gibbs Function G or Gibbs Free Energy:** Gibbs function (G) was called by Duhem the thermodynamical potential at constant pressure. This is defined by the equation.

$$G = U - TS + PV \dots \dots \dots (6)$$

$$\text{As } F = U - TS, \text{ therefore, we can write } G = F + PV \dots \dots \dots (7)$$

This gives the relation between Gibbs function and Helmholtz function. An enthalpy  $H = U + PV$ . Therefore, equation (6) becomes

$$G = H - TS \quad \text{or} \quad H = G + TS \dots \dots \dots (8)$$

**Enthalpy = Gibbs free energy + latent heat**

(a) For an isothermal process:  $TdS = d(TS)$

(b) For an isobaric process:  $dP = 0$

Hence, if the process is isothermal and isobaric then  $dH = d(TS)$  or  $d(H - TS) = 0$   $dG = 0$  or  $G = a$  constant where  $G = H - TS$  is known as **thermodynamic potential at constant pressure; or Gibbs function or Gibbs free energy**.

**Significance of Thermodynamic Potentials:** A mechanical system is said to be in stable equilibrium when the potential energy of the system is minimum. It means that the system must proceed in such a direction so as to acquire minimum potential energy. This what we observe in nature, viz. water flows from a higher level to lower level, electric current flows from higher to lower potential, heat flows from higher to lower temperature, a body falls from higher to lower potential due to gravitational field and so

on. In thermodynamics, the behavior of internal energy (U), enthalpy (H), Helmholtz free energy (F), and Gibbs free energy (G) is similar to potential energy in mechanics. As we have seen, the direction of isothermal-isochoric process is to make Helmholtz free energy (F) minimum. In isothermal isobaric process, Gibbs free energy (G) tends to be minimum. In an isobaric-adiabatic process, the enthalpy (H) tends to be minimum. Since the four functions U, F, H and G play in thermodynamics the same role as played by potential energy in mechanics, they are called **thermodynamic potentials**.

### Relations of thermodynamical potentials with their variables :

The four quantities U (S, V), F (T, V), H (S, P) and G(P, T) are called thermodynamic potentials because the thermodynamic variables S, T, P and V can be derived from them by their differentiations with respect to the independent variables associated with them.

#### 1. Thermodynamical potential U(S, V):

According to first and second law of thermodynamics, Change in internal energy,  $dU = dQ - PdV$  Or  $dU = TdS - PdV$  since  $dQ = TdS$

Taking partial differentials of internal energy U with respect to variable S (entropy), we have

$$\left(\frac{\partial U}{\partial S}\right)_V = T \text{ and } \left(\frac{\partial U}{\partial V}\right)_S = -P \text{ ----- (1)}$$

These are the relations connecting the internal energy U with thermodynamical variables S, V, T and P.

Since dU is a perfect differential (i.e. U is a single valued), we have

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V\right] = \left[\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S\right] \text{ or } \left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial P}{\partial S}\right)_V \text{ ..... (2)}$$

This is Maxwell's first thermodynamical relation.

#### 2. Thermodynamic Potential F(T, V):

The Helmholtz function or Helmholtz free energy is given by  $F = U - TS$   $\therefore dF = d(U - TS) = dU - TdS - SdT$

$$\text{But } dU = TdS - PdV$$

$$\therefore dF = -PdV - SdT$$

Taking partial differential of Helmholtz function F with respect to T and V, we get

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial F}{\partial V}\right)_T = -P \text{ ----- (3)}$$

Since dF is a perfect differential,

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T}\right)_V\right] = \left[\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V}\right)_T\right] \text{ or } \left(\frac{\partial S}{\partial V}\right)_T = - \left(\frac{\partial P}{\partial T}\right)_V \text{ ..... (4)}$$

This is Maxwell's second thermodynamical relation.

#### 3. Thermodynamic Potential H(S, P):

The enthalpy (H) is given by  $H = U + PV$  Differentiating

$$dH = dU + PdV + VdP \text{ but } dU = TdS - PdV$$

$$\therefore dH = TdS + VdP$$

Taking partial differential of enthalpy H with respect to S and P, we get

$$\left(\frac{\partial H}{\partial S}\right)_P = T \text{ and } \left(\frac{\partial H}{\partial P}\right)_S = V \text{ ----- (5)}$$

Since dH is a perfect differential,

$$\left[\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial S}\right)_P\right] = \left[\frac{\partial}{\partial S} \left(\frac{\partial H}{\partial P}\right)_S\right] \text{ or } \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \text{ ..... (6)}$$

This is Maxwell's third thermodynamical relation.

**4. Thermodynamic Potential G (P, T):** The Gibbs function (G) is given by

$$G = H - TS$$

Differentiating, we get

$$dG = dH - TdS - SdT \quad \text{but } dH = TdS + VdP$$

$$\therefore dG = VdP - SdT$$

Taking partial differential of Gibbs function G with respect to P and T, we get

$$\left(\frac{\partial G}{\partial P}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S \text{ ----- (7)}$$

Since dG is a perfect differential,

$$\left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P}\right)_T\right] = \left[\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T}\right)_P\right] \text{ or } \left(\frac{\partial V}{\partial T}\right)_P = - \left(\frac{\partial S}{\partial P}\right)_T \text{ ..... (8)}$$

This is Maxwell's fourth thermodynamical relation.

Thus, the thermodynamical variables S, T, P and V can be written by using equations (1),(3), (5) and (7).

$$\begin{aligned} S &= - \left(\frac{\partial G}{\partial T}\right)_P = - \left(\frac{\partial F}{\partial T}\right)_V \\ T &= \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P \\ P &= - \left(\frac{\partial U}{\partial V}\right)_S = - \left(\frac{\partial F}{\partial V}\right)_T \\ V &= \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T \end{aligned}$$

These equations give the values of thermodynamical variables in terms of thermodynamical potentials.

**First order phase transitions:** The changes of phase which take place at constant temperature and pressure and in which heat either absorbed or evolved during change of phase are called **first order phase order phase transitions**. In first order phase order phase transitions, the entropy and density (or volume) change. The Gibbs function G remains constant in both phases; while its derivative with respect to temperature and pressure is discontinuous at transition point.

Consider an enclosure containing a liquid and its saturated vapour in equilibrium. If this system undergoes an isothermal, isobaric change, then

$$g_1 = g_2 \text{ ..... (1)}$$

Let the temperature of the system be increased from T to T + dT. For equilibrium

$$g_1 + dg_1 = g_2 + dg_2 \text{ ..... (2) Or}$$

$$dg_1 = dg_2 \dots \dots \dots (3)$$

If the condition of saturation is satisfied,

$$\left(\frac{dg_1}{dT}\right)_{sat} = \left(\frac{dg_2}{dT}\right)_{sat} \dots \dots \dots (4)$$

The pressure also changes from P to P+ dP,

$$\therefore dg_1 = \left(\frac{\partial g_1}{\partial T}\right)_P dT + \left(\frac{\partial g_1}{\partial P}\right)_T dP \dots \dots \dots (5) \quad \text{Or}$$

$$\left(\frac{\partial g_1}{\partial T}\right) = \left(\frac{\partial g_1}{\partial T}\right)_P + \left(\frac{\partial g_1}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right) \dots \dots \dots (6)$$

But, for a unit mass,

$$dG = VdP - SdT \dots \dots \dots (7)$$

$$\therefore \left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

Substituting these values in equation (6)

$$\left(\frac{dg_1}{dT}\right)_{sat} = -S_1 + V_1 \left(\frac{\partial P}{\partial T}\right)_{sat} \quad \text{Similarly} \quad \left(\frac{dg_2}{dT}\right)_{sat} = -S_2 + V_2 \left(\frac{\partial P}{\partial T}\right)_{sat}$$

Substituting these values in equation (4)

$$-S_1 + V_1 \left(\frac{\partial P}{\partial T}\right)_{sat} = -S_2 + V_2 \left(\frac{\partial P}{\partial T}\right)_{sat} \quad \text{or}$$

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{S_2 - S_1}{V_2 - V_1} \quad \text{But } S_2 - S_1 = \frac{dQ}{T} = \frac{L}{T}$$

$$\therefore \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \dots \dots \dots (7)$$

**Equation (7) is Clausius – Clapeyron latent heat equation**

**Second order phase transitions: Ehrenfest's Equations :**

Some recent investigations have revealed that during phase change there is no transference of heat and there is no change of volume. It has been found in the case of transition from liquid helium I to liquid helium II, that there is no transfer of heat and no change in volume. Such transitions are called second order phase transitions. Second order phase transitions can be defined as the phenomenon that takes place with no change in entropy and volume at constant temperature and pressure.

Example : The examples of second order phase transitions are:

1. Transition of liquid helium I to liquid helium II, at λ point (2.19 K)
2. Transition of a ferromagnetic material to a paramagnetic material at the Curie point..
3. Transition of a superconducting metal into an ordinary conductor in the absence of a magnetic field
4. Order-disorder transitions in chemical compounds and alloys.

In the case of second-order phase transitions there is no discontinuity of  $\left(\frac{\partial G}{\partial P}\right)_T$  and  $\left(\frac{\partial G}{\partial T}\right)_P$

However, the second order derivatives change discontinuously. For a phase transition

$$g_1 = g_2 \Rightarrow g_2 - g_1 = 0 \dots \dots \dots (1)$$

$$-\left(\frac{\partial g_2}{\partial T}\right)_P + \left(\frac{\partial g_1}{\partial T}\right)_P = S_2 - S_1 = 0 \dots \dots \dots (2)$$

$$\left(\frac{\partial g_2}{\partial T}\right)_P - \left(\frac{\partial g_1}{\partial T}\right)_P = V_2 - V_1 = 0 \dots\dots\dots (3)$$

$$\text{Also, } C_P = T \left(\frac{\partial S}{\partial T}\right)_P$$

$$\frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P = \frac{\partial}{\partial T} \left[ - \left(\frac{\partial g}{\partial T}\right)_P \right] = - \left(\frac{\partial^2 g}{\partial T^2}\right)_P \dots\dots\dots (4)$$

$$K = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \Rightarrow KV = - \left(\frac{\partial V}{\partial P}\right)_T = -\frac{\partial}{\partial P} \left(\frac{\partial g}{\partial P}\right)_T \text{ Or}$$

$$KV = - \left(\frac{\partial^2 g}{\partial P^2}\right)_T \dots\dots\dots (5)$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \alpha V = \left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial}{\partial T} \left(\frac{\partial g}{\partial P}\right)_T \text{ or}$$

$$\alpha V = \frac{\partial^2 g}{\partial T \partial P} \dots\dots\dots (6)$$

Here K is the isothermal compressibility and is the volume coefficient of expansion. From equation (4)

$$\frac{C_{P_1}}{T} = \left(\frac{\partial^2 g_1}{\partial T^2}\right)_P \dots\dots\dots (7) \text{ and } \frac{C_{P_2}}{T} = \left(\frac{\partial^2 g_2}{\partial T^2}\right)_P \dots\dots\dots (8)$$

Subtracting (8) from (7)

$$\left(\frac{\partial^2 g_2}{\partial T^2}\right)_P - \left(\frac{\partial^2 g_1}{\partial T^2}\right)_P = \frac{C_{P_1}}{T} - \frac{C_{P_2}}{T} \dots\dots\dots (9)$$

Similarly from equation (5) and (6)

$$\left(\frac{\partial^2 g_2}{\partial P^2}\right)_T - \left(\frac{\partial^2 g_1}{\partial P^2}\right)_T = V(K_1 - K_2) \dots\dots\dots (10)$$

$$\left(\frac{\partial^2 g_2}{\partial T \partial P}\right) - \frac{\partial^2 g_1}{\partial T \partial P} = V(\alpha_2 - \alpha_1) \dots\dots\dots (11)$$

For second order phase transitions, there is no change in entropy and volume.

$$\therefore S_1 = S_2 \quad (\text{at constant temperatures } T \text{ and pressure } P)$$

$$\therefore S_1 + dS_1 = S_2 + dS_2 \quad (\text{at temp. } T + dT \text{ and pressure } P + dP)$$

$$\therefore dS_1 = dS_2 \dots\dots\dots (12)$$

But

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad \text{Or}$$

$$dS = \frac{C_P}{T} \cdot dT - \left(\frac{dV}{dT}\right)_P dP$$

$$dS = \left(\frac{C_P}{T}\right) dT - V\alpha_1 dP$$

$$dS_1 = \left(\frac{C_{P_1}}{T}\right) dT - V\alpha_1 dP \quad \text{and} \quad dS_2 = \left(\frac{C_{P_2}}{T}\right) dT - V\alpha_2 dP$$

$$\therefore \left(\frac{C_{P_1}}{T}\right) dT - V\alpha_1 dP = \left(\frac{C_{P_2}}{T}\right) dT - V\alpha_2 dP$$

$$\therefore \left(\frac{dP}{dT}\right) = \frac{C_{P_2} - C_{P_1}}{TV(\alpha_2 - \alpha_1)} \text{----- (13)}$$

Similarly by assuming  $V_1 = V_2$  for second order phase transition,

$$\therefore V_1 = V_2 \quad (\text{at constant temperatures } T \text{ and pressure } P)$$

$$\therefore V_1 + dV_1 = V_2 + dV_2 \quad (\text{at temp. } T + dT \text{ and pressure } P + dP)$$

$$\therefore dV_1 = dV_2 \quad \dots \dots \dots (14) \quad \text{But}$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$dV = V\alpha dT - VKdP$$

$$dV_1 = V\alpha_1 dT - VK_1 dP \quad \text{and} \quad dV_2 = V\alpha_2 dT - VK_2 dP$$

$$\therefore V\alpha_1 dT - VK_1 dP = V\alpha_2 dT - VK_2 dP$$

$$\therefore \frac{dP}{dT} = \left(\frac{\alpha_2 - \alpha_1}{K_2 - K_1}\right) \dots \dots \dots (15)$$

Equations (13) and (15) are called **Ehrenfest's Equations**. These equations represent the condition of equilibrium between the two phases.

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